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(71) Applicant: GENERAL ELECTRIC COMPANY  
[US/US]; One River Road, Schenectady, NY 12301 (US)

(72) Inventors: BERZINIS, Albin, P.; RR#7, BOX 38AAA,  
Marietta, OH 45750 (US). PIERRE, Jean, R.; Rue des  
Trois Bonniers 13, B-5081 Saint-Denis (BE).

(74) Agents: HARRINGTON, Mark, F. et al.; Harrington &  
Smith, LLP, 1809 Black Rock Turnpike, Fairfield, CT  
06432-3504 (US).

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(54) Title: PC/ASA COMPOSITION HAVING IMPROVED NOTCHED IZOD AND REDUCED GATE BLUSH

(57) Abstract: A thermoplastic composition having reduced gate blush comprises: a polycarbonate; an acrylonitrile-butylacry-  
late-styrene resin; and a high molecular weight acrylic copolymer processing aid. The high molecular weight processing aid is an  
acrylic copolymer, preferably selected from the group consisting of styrene-acrylonitrile, methylmethacrylate-butylmethacrylate,  
methylmethacrylate-ethylacrylate, and butylmethacrylate-methacrylate copolymers.

## PC/ASA COMPOSITION HAVING IMPROVED NOTCHED IZOD AND REDUCED GATE BLUSH

### Field of the Invention

The present invention relates to thermoplastic compositions  
5 comprising a blend of polycarbonate, a grafted emulsion rubber with a glass  
transition temperature of less than 0 °C and a mean particle size of 50-1000  
nm, preferably 50-600 nm, which can be a graft acrylonitrile-butylacrylate-  
styrene (ASA) resin, a graft acrylonitrile-butadiene-styrene (ABS) resin or a  
10 graft acrylonitrile-(ethylene-propylene-diene)-styrene (AES) resin, one or two  
amorphous non crosslinked linear copolymers such as SAN, AMSAN, PMMA  
or MMA-SAN and further containing a gate blush reducing component  
selected from the group consisting of high molecular weight polymers  
consisting of copolymers of styrene-acrylonitrile or alkylacrylates.

### Background of the Invention

15 There are many references in the prior art to blends of polycarbonate  
and ABS, the first significant patent reference in this field being the  
Grabowski U.S. Pat. No. 3,130,177. There are also many references in the prior  
art to blends of polycarbonate and ASA to improve weathering properties.  
As improvements on the original Grabowski patent were developed, attention  
20 was focussed on the weld line strength problem, which characterized certain  
of these blends. In the Margotte et al. U.S. Pat. No. 3,988,389, the weld line  
strength of a polycarbonate/ABS blend is said to be improved by using a very  
specific graft ABS formulation having a narrowly defined graft ratio, rubber  
particle size, rubber content, and the like.

25 Insofar as the use of poly (alkyl methacrylates) in rubber modified  
polycarbonates is concerned, British Patent 1,182,807 describes a blend of

athermoplastic aryl polycarbonate and a poly(methylmethacrylate) which may optionally include a minor proportion of a "rubbery polymeric material." Examples of the latter "rubbery polymeric material" include SBR and nitrile rubbers as well as graft polymers, primarily rubbery acrylate copolymers. 5 Graft ABS, and more particularly, high rubber graft/styrene-acrylonitrile (SAN) blends are not mentioned or suggested.

Weatherable thermoplastic compositions based on poly(butyl acrylate) rubbers grafted with styrene-acrylonitrile (ASA) are currently used for exterior automotive parts such as mirror housings, wind deflectors, front 10 grills etc. Polycarbonate (PC)/ASA blends provide long term heat resistance with good weathering characteristics. Because major applications are for unpainted exterior parts, aesthetics is very critical. Polymer blends based on PC often suffer from a "gate blush" defect, which is manifested as a dull zone on the surface of the part adjacent to the gate. The severity of this effect is 15 somewhat dependent on the design of the gating into the part and also upon the shear stress applied during the injection molding process. This suggests that this defect is related to the distortion of the complex blend morphology during the injection process through the effect of the melt rheology of the individual blend components.

## 20 Summary of the Invention

The present invention relates to the use of high molecular weight processing aid polymers (SAN copolymers, Acrylic copolymers) to produce weatherable molded parts with good aesthetics, low gate blush, improved 25 notched Izod impact characteristics and good property retention under long term thermal aging or weathering.

In the present invention, it has been discovered that the use of up to about 5 per cent by weight of a high weight average molecular weight acrylic

or styrene-acrylonitrile copolymer, has a dramatic effect on the gate blush and improves the notched Izod impact of blends of polycarbonate, such as bisphenol A polycarbonate, and graft polymers of acrylate styrene acrylonitrile (ASA), acrylonitrile-butadiene-styrene (ABS) or acrylonitrile-  
5 (ethylene-propylene-diene)-styrene (AES), preferably those graft polymers formulated with a high rubber graft and a rigid phase comprising one or two amorphous non crosslinked linear copolymers such as SAN, AMSAN, PMMA or MMA-SAN.

- A composition having reduced gate blush and an improved notched  
10 Izod is provided for by a thermoplastic composition comprising:
- a) polycarbonate;
  - b) a grafted rubber preferably with a glass transition temperature of less than 0 °C and preferably with a mean particule size of 50-1000 nm, preferably 50-600nm, which can be a graft acrylonitrile-  
15 butylacrylate-styrene (ASA) resin, a graft acrylonitrile-butadiene-styrene (ABS) resin or a graft acrylonitrile-(ethylene-propylene-diene)-styrene (AES) resin and a rigid phase comprising one or two amorphous non crosslinked linear copolymers such as SAN, AMSAN, PMMA or MMA-SAN; and
  - 20 c) a high molecular weight acrylic copolymer processing aid.

#### Detailed Description of the Invention

As mentioned above in the summary portion of this Specification, the present invention relates generally to blends of ASA copolymer with polycarbonate, which blends further contain up to about 5 % by weight  
25 (based on the end product) of a high weight average molecular weight acrylic copolymer. As used herein when the phrase "up to about" is used in conjunction with a maximum amount and no specifically stated minimum

amount the phrase should be taken to mean "from slightly greater than zero up to about."

The ASA comprises an acrylic monomer such as acrylonitrile, substituted acrylonitrile, and/or an acrylic acid ester, exemplified by alkyl acrylates such as ethyl acrylate and methyl methacrylate.

Examples of the cyano-containing alkenyl nitrile monomers include acrylonitrile, ethacrylonitrile, methacrylonitrile, alpha -chloroacrylonitrile, beta -chloroacrylonitrile, alpha -bromoacrylonitrile, and beta -bromoacrylonitrile, while examples of the acrylic acid esters include methyl acrylate, alkyl methacrylate, ethyl acrylate, butyl acrylate, propyl acrylate, isopropyl acrylate and mixtures thereof. The preferred acrylic monomer is an alkenyl nitrile, particularly acrylonitrile. In a further preferred embodiment, the grafting monomers which form the ASA resin are essentially free of methylmethacrylate, i.e., the grafting monomers containing less than about 5 weight percent methyl methacrylate.

Generally the acrylate styrene acrylonitrile (ASA) component of the composition of the present invention is produced by a process that comprises the steps of emulsion polymerizing at least one alkyl acrylate monomer in the presence of from about 0.05% to about 10% by weight of a polyfunctional crosslinking monomer to form an aqueous latex of crosslinked acrylic elastomer particles, thereafter emulsion polymerizing a charge of styrene and acrylonitrile monomers in the presence of a crosslinking agent and the crosslinked latex particles to crosslink the styrene acrylonitrile charge, and thereafter adding a monomeric charge of styrene and acrylonitrile which does not contain a crosslinking agent but which does contain an initiator to polymerize the monomers and form a linear styrene-acrylonitrile polymer. The final product that is formed has impact and weather resistance and

comprises from about 10 to 50% by weight of the crosslinked acrylic elastomer, from about 5 to 35% by weight of the crosslinked styrene-acrylonitrile copolymer surrounding and penetrating the crosslinked acrylic elastomer, and from about 15 to 85% by weight of the polymerized linear  
5 styrene acrylonitrile.

In greater detail, now, the elastomer particles that are utilized in preparing the particles of this invention are made by means of conventional aqueous emulsion procedures well known to those skilled in the art of using emulsifiers and water-soluble catalysts.

10 Thus, in conducting the aqueous emulsion polymerization step leading to the preparation of these elastomer particles, there is preferably first prepared a monomer charge comprising an aqueous emulsion containing about 10 to 50%, by weight, of one or more monomers, the identity of which will be described in detail hereinbelow, and from 0.2 to 2.0% by weight of a  
15 suitable emulsifier. From about 0.05 to 2.0% by weight of the monomer mixture, of a water-soluble catalyst, such as ammonium, sodium or potassium persulfate, hydrogen peroxide or a redox system, such as a mixture of a persulfate with an alkali metal bisulfite, thiosulfate or hydrosulfite, is introduced, and the mixture is then heated at a temperature of from about 40°  
20 to 95°C for a period of about 0.5 to 8 hours.

The acrylic elastomer particles used in preparing the particles of this invention comprise crosslinked acrylic polymers or copolymers having a T<sub>g</sub>, i.e., a glass transition temperature, of less than about 25°C which can be polymerized by means of free radical initiated emulsion techniques. These  
25 acrylic elastomer particles should be crosslinked so that they can retain their size and shape during subsequent polymer processing steps. This crosslinking can be achieved during the polymerization of the elastomer if a

polyfunctional ethylenically unsaturated monomer is included in the polymerization recipe. As used in this disclosure, the term "crosslinked" denotes a polymer that at ambient temperatures is substantially insoluble in such organic solvents as tetrahydrofuran or cyclohexanone.

5           Examples of acrylic elastomers that can be used include the crosslinked polymers of the C<sub>2</sub>-C<sub>10</sub> alkyl acrylate and the C<sub>8</sub>-C<sub>22</sub> alkyl methacrylate monomers, preferably the C<sub>4</sub>-C<sub>8</sub> alkyl acrylates, such as poly(n-butyl acrylate), poly(ethyl acrylate) and poly(2-ethyl hexylacrylate). At least one acrylate monomer is utilized in this step. If desired, the monomer charge may  
10       contain small amounts, i.e., 1% to 20% by weight of the amount acrylate monomer, of optional monomers including styrene, acrylonitrile, methacrylonitrile, methyl methacrylate, methacrylic acid, acrylic acid, vinylidene chloride, vinyl toluene and any other ethylenically unsaturated monomer copolymerizable with the acrylate monomer selected for use.

15           In order to crosslink the acrylate monomer from about 0.05% to about 10% by weight (preferably 0.1% to 5%) based on the weight of acrylate monomer, of at least one crosslinking agent is used. This crosslinking agent is for the purposes of this composition a di- or poly-functional ethylenically unsaturated monomer having at least one vinyl group. As is well known in  
20       the art the vinyl groups on the crosslinking monomer can be the same (e.g. divinyl benzene, trimethylol propane triacrylate, etc.) or different, (e.g., allyl methacrylate, diallyl fumarate, diallyl maleate, etc.) Examples of other suitable crosslinking monomers which are known to persons in the art and which can be used are 1,3-butylene dimethacrylate, diethylene glycol  
25       dimethacrylate, ethylene glycol dimethacrylate, trimethylolpropane trimethacrylate, methylene bisacrylamide, diethylene glycol diacrylate, ethylene glycol diacrylate, divinyl ether, diallyl phthalate, divinyl sulfone, divinyl sorbitol, triethylene glycol dimethacrylate, trimethylene glycol

diacrylate, butylene glycol diacrylate, pentamethylene glycol diacrylate, glyceryl triacrylate, octylene glycol diacrylate, trimethylolpropane triacrylate, the tetra-acrylate ester of pentaerythritol and various diallyl phosphonates.

Optimum results are obtained by the use of a crosslinked copolymer  
5 containing from about 95 to 99.9% by weight of n-butyl acrylate and from about 0.1 to 5%, by weight, of butylene glycol diacrylate.

The emulsifier which is used is at least one of the following conventional types: an anionic emulsifier, e.g., the C<sub>2</sub>-C<sub>22</sub> carboxylic acids, the sulfates or, sulfonates, of C<sub>6</sub>-C<sub>22</sub> alcohols or alkyl phenols; a non-ionic  
10 emulsifier, e.g., the addition products of alkylene oxides to fatty acids, amines or amides; a combination of the foregoing anionic and non-ionic emulsifiers; or the cationic emulsifiers, e.g., a quaternary ammonium containing compound. The amount of emulsifier should be present from about 0.5% to about 5% by weight in the emulsion.

Moreover, in a preferred embodiment of the process of this invention,  
15 it has been found that regardless of the particular emulsifier being utilized in preparing the rubber polymer latex, its polymerization in large scale commercial equipment is greatly facilitated by introducing the monomer charge to the system in several portions over a period of from 1 to 3 hours.  
20 Thus, where this is not done and the total monomer charge is introduced in one portion, the resulting exothermic polymerization reaction often becomes virtually uncontrollable leading to overheating which, in turn, may set up, i.e., coagulate, the resulting polymer latex. However, by dividing the monomer charge and introducing it in about several portions, the resulting  
25 polymerization reaction remains controllable and overheating and coagulation can be prevented.



An initiator is also present in the emulsion in an amount ranging from about 0.005% to 2% by weight of the acrylate monomer. Suitable for use are water-soluble peroxide compounds, e.g., hydrogen peroxide and alkali metal and ammonium persulfates, oil soluble organic peroxides and azo compounds, e.g., benzoyl peroxide, azo-bis-isobutyronitrile and the like, used singly or in combination. Redox catalysts, e.g., mixtures of peroxide catalysts with reducing agents, such as hydrazine, alkali metal bisulfites, thiosulfates, and hydrosulfites, and soluble oxidizable sulfoxyl compounds can also be used.

A chain transfer agent such as an alkyl mercaptan, e.g., t-dodecyl mercaptan, toluene, xylene, chloroform, halogenated hydrocarbons and the like may also be used.

A buffer to keep the pH at 7.0 or higher is a final component of the emulsion.

The next step in the preferred embodiment of preparing the ASA polymer used in the compositions of the present invention is the emulsion polymerization of a mixture of styrene and acrylonitrile in the presence of a minor portion of at least one difunctional or polyfunctional crosslinking monomer to form a crosslinked styrene-acrylonitrile polymer. This emulsion polymerization is carried out in the presence of the crosslinked acrylic elastomer by adding the styrene-acrylonitrile charge to the previously prepared aqueous emulsion of crosslinked acrylate elastomer. The amount of styrene-acrylonitrile which is added ranges from 5 to 35% of the weight of the final product that will be produced whereas the crosslinked acrylate elastomer is present from about 10% to 50% based upon the weight of the final product which will be formed.

The monomer charge of styrene-acrylonitrile can comprise from about 50/50 to 85/15 weight parts of styrene to acrylonitrile with the preferred ratio being 76/24. If desired, minor amounts e.g., below about 20% by weight, of optional monomers can be included. Examples are t-butyl styrene, p-  
5 chlorostyrene, alpha-methyl styrene, methyl methacrylate, alkyl acrylate, vinylidene chloride, ethylene, propylene, isobutylene and other ethylenically unsaturated compounds copolymerizable with styrene and acrylonitrile.

The crosslinking agent, emulsifiers, initiators and chain transfer agents discussed in the previous step can also be used in this step in the same  
10 amounts to form the crosslinked styrene-acrylonitrile on crosslinked acrylate elastomer.

If desired, the two steps described above may be reversed in sequence.

After the emulsion polymerization of the crosslinked styrene-acrylonitrile polymer onto the crosslinked acrylic elastomer or the reverse  
15 sequence of these two steps has been accomplished, the final step of the present invention is performed. This is the formation of a linear styrene-acrylonitrile polymer which is not substantially grafted onto the crosslinked acrylic elastomer-crosslinked styrene-acrylonitrile copolymers. The amount of linear styrene-acrylonitrile polymer which is grafted is less than 30 weight  
20 percent, preferably less than 20 weight percent. This third step may be accomplished by either suspension or emulsion polymerization of a charge of styrene and acrylonitrile monomers having the same general composition as the styrene and acrylonitrile charge used in the previous step in the absence of a crosslinking monomer. The combined amounts of styrene and  
25 acrylonitrile utilized in this step will vary from 15-85% by weight of the final product. The same emulsifiers, initiators, chain transfer agents and optional

monomers utilized in previous steps may be used in this final polymerization procedure.

If suspension polymerization is chosen the suspending agent can be methyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, carboxymethyl cellulose, talc, clay, polyvinyl alcohol, gelatin and the like. Preferred for this purpose is hydroxypropyl methyl cellulose which should, preferably, have a viscosity of at least about 3,000 and, preferably, about 15,000 cps. As determined, at 20 °C, with a 2%, by weight, aqueous solution of the polymer in an Ubbelohde viscometer according to ASTM Procedures D-1347-64 and D-2363-65T.

Other additives can be used in forming the linear styrene-acrylonitrile matrix to confer desired properties upon the final product. Included are conventional light, thermal and ultraviolet light stabilizers, antioxidants, dyes, pigments, mineral additives and fillers and reinforcing fillers.

Polycarbonates are a special class of polyesters derived from the reaction of carbonic acid derivatives with aromatic, aliphatic, or mixed diols. They may be produced by the reaction of phosgene with a diol in the presence of an appropriate hydrogen chloride receptor or by a melt transesterification reaction between the diol and a carbonate ester. Polycarbonate can be made from a wide variety of starting materials, however, the principal polycarbonate produced commercially is bisphenol A polycarbonate, a polycarbonate made by reacting bisphenol A with phosgene by condensation.

For a more complete discussion of the chemistry of polycarbonates, one may refer to The Kirk-Othmer Encyclopedia of Chemical Technology, Third Edition (1982), Vol. 18, pp. 479-494. The article contained therein by D. W. Fox is incorporated herein by reference in its entirety.

Polymethylmethacrylate (PMMA) is produced by the polymerization of methyl methacrylate monomer, and may be derived by (1) the reaction of acetone cyanohydrin, methanol and sulfuric acid or (2) the oxidation of tert-butyl alcohol to methacrolein and then to methacrylic acid followed by the esterification reaction with methanol. PMMA homopolymer exists in its pure form only theoretically and is generally available commercially as a mixture of the homopolymer and various copolymers of methyl methacrylate and C<sub>1</sub>-C<sub>4</sub> alkyl acrylates, such as ethyl acrylate.

Preferably, the compositions according to the present invention contain from about 5 to about 95 weight percent polycarbonate, preferably from about 10 to about 90 weight percent polycarbonate, more preferably from about 20 to about 80 weight percent polycarbonate, and most preferably from about 25 to about 75 weight percent polycarbonate; from about 5 to about 70 weight percent ASA copolymer, preferably from about 10 to about 60 weight percent ASA copolymer, more preferably from about 15 to about 40 weight percent ASA copolymer and most preferably from about 12 to about 30 weight percent ASA copolymer; and from about 1 to about 10 weight percent processing aid, preferably from about 1.5 to about 8 weight percent processing aid, more preferably from about 2 to about 7 weight percent processing aid and most from about 2.5 to about 6 weight percent processing aid where the processing aid is a high weight average molecular weight acrylic copolymer selected from the group consisting of styrene-acrylonitrile, methylmethacrylate-butylmethacrylate, methylmethacrylate-ethylacrylate, and butylmethacrylate-methacrylate.

The weight average molecular weight (measured by GPC of solutions in chloroform using a calibration curve based on analysis of monodisperse fractions of reference polystyrene of known molecular weight) of the processing aid is above 400K daltons, preferably above 500K daltons, more

preferably above 550K daltons and most preferably above 600K daltons. This invention has been described in connection with certain specific embodiments, but it should not be limited to the specific embodiments described herein.

## 5 Examples

An ASA was prepared by emulsion polymerization from a crosslinked butylacrylate (BA) rubber of broad particle size distribution (from 50 nm to 1000 nm, preferably from 50 to 700 nm) to which was grafted SAN (the AN composition in copolymer from 15 to 35%, preferably from 25 to 30%) to a  
10 final BA content of 30-70%, preferably from 45-60%. Blends with Polycarbonate were obtained by first dry blending Polycarbonate powder with ASA powder, SAN suspension beads, high molecular weight processing aid powder and appropriate additives in a high speed mixer (Henschel or Papienmeier), followed by extrusion through a co-rotating intermeshing twin-  
15 screw extruder using a temperature profile from 200 to 260C. The granulated products so obtained were molded using a multicavity ISO tool using melt temperature varying from 250C to 260C and a mould temperature around 60C.

The following processing aids were evaluated:

20 Blendex 869: SAN copolymer; Mw(\*)=610K (GE-Specialty Chemicals)

Metablen P552: Methylmethacrylate-butylacrylate copolymer; Mw(\*)=930K (ATO)

Paraloid K120N: Methylmethacrylate-ethylacrylate copolymer; Mw(\*)=720K(Rohm and Haas)

Kane Ace X210: Methylmethacrylate-butylacrylate copolymer;  
Mw(\*)=830K(Kaneka)

Typical resin compositions comprise:

- (i) 50-90% polycarbonate (Mw(\*)=25,000 to 200,000);
- 5 (ii) 10-40% grafted polybutylacrylate rubber;
- (iii) 0-40% SAN copolymer (Mw(\*)=60,000 to 300,000)
- (iv) 2.5-5% High molecular weight processing aid (Mw(\*)=400,000 to  
1,500,000) based on SAN or Acrylic copolymers.
- (v) Lubricants, antioxidants and light stabilisers
- 10 (vi) Fillers, pigments and dyes

(\*) Mw measured by GPC in Chloroform using monodisperse polystyrene calibration.

Performed experiments:

15 The tables 1 and 2 show results obtained on PC/ASA blends containing 60 phr (parts per hundred parts resin) and 72 phr Polycarbonate and modified with 3.5phr of Blendex 869 SAN, Metablen P552, Paraloid K120N and Kane Ace X210 Acrylic processing aids. Data of formulations containing no processing aid are also given for comparison.

20 It appears that both SAN and Acrylic processing aids improve the gate. Addition of processing aids also increases the notched Izod impact of the blends. Moreover, all other properties are retained.

**TABLE 1**

Composition (phr)	#1	#2	#3	#4	#5
PC (Mw=61K)	30	30	30	36	36
PC (Mw=43K)	30	30	30	36	36
ASA-HRG	18	18	18	12	12
SAN	22	18.5	18.5	16	16
Blendex 869(SAN; Mw=612K)		3.5			3.5
Metablen P552(Acrylic; Mw=932K)			3.5		
Paraloid K120N (Acrylic; M=721K)				3.5	
Kane Ace X210 (Acrylic; Mw=827K)					3.5
Titanium dioxide	5	5	5	5	5
Gate blush?	Bad	Good	Good	Good	Good
Vicat B/120(C)	119	122	120	120	121
Melt volume rate- 260C/5Kg (cc/10mn)	25	16	18	18	17
Notched izod impact@RT (KJ/m2)	40	65	56	50	61
Notched izod impact@-30C (KJ/m2)	9	16	13	14	17
Multiaxial impact -Energy@max(J)	98	90	95	95	92
Tensile strength @yield(Mpa)	56	56	54	57	57
% Elongation @ break	114	90	110	96	97
Tensile modulus (Mpa)	2410	2450	2320	2440	2480

**TABLE 2**

Composition (phr)	#6	#7	#8	#9	#10
PC (Mw=61K)	36	36	36	36	36
PC (Mw=43K)	36	36	36	36	36
ASA-HRG	12	12	12	12	12
SAN	16	12.5	12.5	12.5	12.5
Blendex 869(SAN; Mw=612K)		3.5			3.5
Metablen P552(Acrylic; Mw=932K)			3.5		
Paraloid K120N (Acrylic; M=721K)				3.5	
Kane Ace X210 (Acrylic; Mw=827K)					3.5
Titanium dioxide	5	5	5	5	5
Gate blush?	Bad	Good	Good	Good	Good
Vicat B/120(C)	130	132	131	131	131
Melt volume rate- 260C/5Kg (cc/10mn)	22	15	15	16	15
Notched izod impact@RT (KJ/m2)	38	51	54	50	59
Notched izod impact@-30C (KJ/m2)	13	19	17	16	18
Multiaxial impact -Energy@max(J)	94	87	102	94	100
Tensile strength @yield(Mpa)	60	58	61	61	59
% Elongation @ break	109	95	122	109	103
Tensile modulus (Mpa)	2480	2450	2410	2440	2400

Table 3 shows that the same conclusions apply to PC/ASA blends based on 45 phr Polycarbonate and 5 phr of all four high molecular weight processing aids considered. The data indicate also that more than 2.5phr are required to completely remove the gate blush. It is important to note that an important die swell was observed during compounding for all compositions containing high molecular weight processing aids.

To test whether bulk melt rheology alone is responsible for the effect of these processing aids on gate blush we compared the effects of the Metablen P-552 and Blendex 869 to that of a dispersion of UHMW Teflon in SAN. The Teflon is commonly added as an anti-drip agent in flame-retardant PC blends and is well known to cause substantial die swell when the blend formulations are extruded or injection molded. The blends described in Table 3 (45% PC, 25% ASA, medium grey pigment) were prepared as described above via extrusion compounding and then were injection-molded into ASTM test specimens. The test result units have been translated into ISO units for more convenience. The results show that while the Teflon additive did result in substantial die swell, it was ineffective in either eliminating gate blush or in improving the notched Izod impact strength of the ASA/PC blends. The beneficial actions of the preferred process aids in ASA/PC blends can not be anticipated from their effect on melt rheology alone.



**TABLE 3**

Composition(phr)	#11	#12	#13	#14	#15	#16	#17
PC (Mw=100K)	45	45	45	45	45	45	45
ASA-HRG	25	25	25	25	25	25	25
SAN	30	27.5	25	27.5	25	29.75	29.5
Blendex 869		2.5	5				
Metablen P552				2.5	5		
Teflon-SAN						0.25	0.5
Carbon black	0.4	0.4	0.4	0.4	0.4	0.4	0.4
TiO2	3.5	3.5	3.5	3.5	3.5	3.5	3.5
Gate blush?	Bad	Mod	Good	Mod	Good	Bad	Bad
HDT-181 Mpa(C)	114	116	117	112	115	115	115
Melt flow index- 260C/5Kg (g/10mn)	59	30	27	41	31	37	35
Notched Izod impact@RT (KJ/m2)	20	49	51	30	49	30	37
Multiaxial impact -Energy@max(J)	48	45	47	48	49	49	49
Tensile strength @yield(Mpa)	59	59	58	58	58	60	60
% Elongation @ break	112	97	110	128	134	110	118
Flexural modulus (Mpa)	2480	2530	2450	2470	2370	2490	2460

Mod= moderate

**TABLE 4**

Composition (phr)	#18	#19	#20	#21
PC (Mw=50K)	33	33	59	59
ASA-HRG	25	25		
ABS-HRG			12	12
SAN	17	12	22	17
PMMA	23	23		
Metablen P552(Acrylic; Mw=932K)		5		5
Carbon black	3	3	1.5	1.5
Titanium dioxide	0.4	0.4		
Gate blush?	Bad	Good	Bad	Good
Vicat B/120(C)	105	106	126	126
Melt volume rate- 260C/5Kg (cc/10mn)	26	18	22	14
Notched izod impact@RT (KJ/m2)	14	17	37	39
Notched izod impact@-30C (KJ/m2)	7	8	13	15

The improvement in aesthetics and impact characteristics is also observed when SAN is prtly replaced by PMMA or when the ASA rubber is replaced by ABS rubber . The blends described in table 4 were prepared as described above via extrusion compounding and injected into ISO test specimens. The  
5 data show that the high MW acrylic processing aid is also effective in eliminating gate blush and increasing the notched izod impact of both types of formulation.

## CLAIMS

Having described the invention that which is claimed is:

1. A thermoplastic composition comprising:
  - a. polycarbonate;
  - 5       b. acrylonitrile-butylacrylate-styrene resin; and
  - c.     a high molecular weight acrylic copolymer processing aid.
2. The composition of claim 1 wherein the notched Izod is at least 50 KJ/m<sup>2</sup>.
3. The composition of claim 1 wherein the high molecular weight acrylic copolymer processing aid is an acrylic copolymer selected from the group  
10       consisting of styrene-acrylonitrile, methylmethacrylate-butylmethacrylate, methylmethacrylate-ethylacrylate, and butylmethacrylate-methacrylate copolymers.
4. The composition of claim 3 wherein the polycarbonate is present in an amount ranging from about 5.0 to about 95.0 weight percent, the  
15       acrylonitrile-butylacrylate-styrene resin is present in an amount ranging from about 5.0 to about 70.0 weight percent and the high molecular weight acrylic copolymer processing aid is present in an amount ranging from slightly greater than zero up to about 5.0 weight percent.
5. The composition of claim 4 wherein the high molecular weight acrylic  
20       copolymer processing aid is a styrene-acrylonitrile copolymer.
6. The composition of claim 4 wherein the high molecular weight acrylic copolymer processing aid is a methylmethacrylate-butylmethacrylate copolymer.

7. The composition of claim 4 wherein the high molecular weight acrylic copolymer processing aid is a methylmethacrylate-ethylacrylate copolymer.
8. The composition of claim 4 wherein the high molecular weight acrylic copolymer processing aid is a butylmethacrylate-methacrylate copolymer.
9. The composition of claim 4 where the weight average molecular weight of the high molecular weight acrylic copolymer processing aid is above 400K daltons.
10. The composition of claim 5 where the weight average molecular weight of the high molecular weight acrylic copolymer processing aid is above 400K daltons.
11. A thermoplastic composition consisting essentially of:
- polycarbonate;
  - an acrylonitrile-butylacrylate-styrene resin; and
  - a high molecular weight acrylic copolymer processing aid.
12. The composition of claim 11 wherein the notched Izod is at least 50 KJ/m<sup>2</sup>.
13. The composition of claim 11 wherein the high molecular weight acrylic copolymer processing aid is an acrylic copolymer selected from the group consisting of styrene-acrylonitrile, methylmethacrylate-butylmethacrylate, methylmethacrylate-ethylacrylate, and butylmethacrylate-methacrylate copolymers.

14. The composition of claim 13 wherein the polycarbonate is present in an amount ranging from about 5.0 to about 95.0 weight percent, the acrylonitrile-butylacrylate-styrene resin is present in an amount ranging from about 5.0 to about 70.0 weight percent and the high molecular weight acrylic copolymer processing aid is present in an amount ranging from slightly greater than zero up to about 5.0 weight percent.
15. The composition of claim 14 wherein the high molecular weight acrylic copolymer processing aid is a styrene-acrylonitrile copolymer.
16. The composition of claim 14 wherein the high molecular weight acrylic copolymer processing aid is a methylmethacrylate-butylmethacrylate copolymer.
17. The composition of claim 14 wherein the high molecular weight acrylic copolymer processing aid is a methylmethacrylate-ethylacrylate copolymer.
18. The composition of claim 14 wherein the high molecular weight acrylic copolymer processing aid is a butylmethacrylate-methacrylate copolymer.
19. The composition of claim 14 where the weight average molecular weight of the high molecular weight acrylic copolymer processing aid is above 400K daltons.
20. The composition of claim 15 where the weight average molecular weight of the high molecular weight acrylic copolymer processing aid is above 400K daltons.
21. A thermoplastic composition having reduced gate blush comprising:
- polycarbonate;
  - an acrylonitrile-butylacrylate-styrene resin; and
  - a high molecular weight acrylic copolymer processing aid.

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(71) Applicant: **GENERAL ELECTRIC COMPANY**  
[US/US]; One River Road, Schenectady, NY 12301 (US).

(72) Inventors: **BERZINIS, Albin, P.**; RR#7, bOX 38AAA,  
Marietta, OH 45750 (US). **PIERRE, Jean, R.**; Rue des  
Trois Bonniers 13, B-5081 Saint-Denis (BE).

(74) Agents: **HARRINGTON, Mark, F.** et al.; Harrington &  
Smith, LLP, 1809 Black Rock Turnpike, Fairfield, CT  
06432-3504 (US).

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(57) Abstract: A thermoplastic composition having reduced gate blush comprises: a polycarbonate; an acrylonitrile-butylacry-, late-styrene resin; and a high molecular weight acrylic copolymer processing aid. The high molecular weight processing aid is an acrylic copolymer, preferably selected from the group consisting of styrene-acrylonitrile, methylmethacrylate-butylmethacrylate, methylmethacrylate-ethylacrylate, and butylmethacrylate-methacrylate copolymers.

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<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 98 08900 A (BASF AG ;WEBER MARTIN (DE); GUENTHERBERG NORBERT (DE)) 5 March 1998 (1998-03-05) page 5, line 25 -page 8, line 30; claim 1	1-5, 9-15, 19-21
A	EP 0 673 971 A (GEN ELECTRIC) 27 September 1995 (1995-09-27) page 2, line 23 - line 25; claim 1	1-21
A	CA 2 067 258 A (MILES INC) 5 December 1992 (1992-12-05) claims 9,10	21
A	EP 0 994 147 A (PREMARK RWP HOLDINGS INC) 19 April 2000 (2000-04-19)  column 10, line 16 - line 24	1,3, 6-11,13, 15-21
<input type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.		
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## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 01/32494

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9808900	A	05-03-1998	DE 19635078 A1	05-03-1998
			AT 190639 T	15-04-2000
			AU 4380497 A	19-03-1998
			BR 9711239 A	17-08-1999
			CN 1228799 A	15-09-1999
			DE 59701282 D1	20-04-2000
			WO 9808900 A1	05-03-1998
			EP 0922073 A1	16-06-1999
			ES 2144879 T3	16-06-2000
			HU 9904126 A2	28-04-2000
			JP 2001501227 T	30-01-2001
			PL 331890 A1	16-08-1999
			SK 22799 A3	10-04-2000
			US 6232397 B1	15-05-2001
EP 0673971	A	27-09-1995	EP 0673971 A1	27-09-1995
			WO 9525772 A1	28-09-1995
CA 2067258	A	05-12-1992	CA 2067258 A1	05-12-1992
EP 0994147	A	19-04-2000	US 2001036557 A1	01-11-2001
			AU 722189 B2	27-07-2000
			AU 4755499 A	11-05-2000
			BR 9904713 A	23-01-2001
			CN 1255428 A	07-06-2000
			EP 0994147 A1	19-04-2000
			HU 9903600 A2	28-10-2000
			JP 3105213 B2	30-10-2000
			JP 2000119541 A	25-04-2000
			NZ 337541 A	22-12-2000
			PL 335994 A1	25-04-2000
			ZA 9905598 A	29-03-2000



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